

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: C08L 67/00, 77/00, C08K 5/00 // (C08K 5/00, 5:3492, 5:54)	A1	(11) International Publication Number: WO 99/02606 (43) International Publication Date: 21 January 1999 (21.01.99)
(21) International Application Number: PCT/NL98/00226 (22) International Filing Date: 22 April 1998 (22.04.98) (30) Priority Data: 1006525 10 July 1997 (10.07.97) NL (71) Applicant (for all designated States except US): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). (72) Inventor; and (75) Inventor/Applicant (for US only): HULSKOTTE, Richerdes, Johanna, Mathilda [NL/NL]; Breijerode 43, NL-6365 CT Schinnen (NL). (74) Agent: ALFENAAR, Marinus; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).	(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, ID, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: HALOGEN-FREE FLAME-RETARDANT THERMOPLASTIC POLYESTER OR POLYAMIDE COMPOSITION (57) Abstract The invention relates to a flame-retardant polyester or polyamide composition that contains a combination of a compound derived from triazine and an organic phosphorus compound. By choosing as the triazine compound a melamine condensation product, for example melam, a UL 94 V-0 and GWFI 960° classification can be obtained for glass-fibre reinforced polyester or polyamide with a relatively low concentration of flame-retardant additives, and without good mechanical properties being affected. Moreover it is unusual that the CTI value can again be brought to 600 Volt for this glass-fibre reinforced polyester or polyamide. In a preferred embodiment use is made of a phosphorous-containing compound containing more than 14 wt.% P. The use thereof with for example melamine cyanurate results in optimum flame-retardant behaviour at a low total concentration of flame-retardant additives. Important additional aspects are improved crystallisation behaviour and a high stiffness.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

- 1 -

HALOGEN-FREE FLAME-RETARDANT THERMOPLASTIC
POLYESTER OR POLYAMIDE COMPOSITION

5

The invention relates to a halogen-free, flame-retardant thermoplastic polyester or polyamide composition that contains a combination of organic phosphorus compound and a nitrogen-containing flame retardant.

Such a composition is known from EP-A-672,717. This describes a flame-retardant polybutylene terephthalate, PBT, composition in which the organic phosphorus compound is a hydroquinone type of aromatic oligo- or polyphosphate and the nitrogen-containing flame retardant is a salt of a triazine derivative with at least one acid of cyanuric acid or isocyanuric acid. In the examples melamine, benzoguanamine and acetoguanamine are used as the triazine derivative. To obtain a UL-94 V-O classification, the compositions contain approx. 20 parts by weight of organic phosphorus compound and at least 8 parts by weight of triazine derivative per 100 parts by weight of PBT. With glass fibre present in the composition the required concentration of flame retardant combination was at least approx. 40 parts by weight per 100 parts by weight of PBT with 30 parts by weight of glass fibre.

Such high concentrations of flame retardant combination have a highly adverse influence on the polymer composition's mechanical and processing properties. For example, a value of at least 50°C was found for the difference between T_m and T_c , T_m = melting point and T_c = crystallisation temperature, measured with differential scanning calorimetry (DSC),

35

- 2 -

for the PBT-based compositions according to the
aforementioned state of the art. For PBT without a
flame retardant this difference is 35-40°C resulting in
a shorter cycle time in injection moulding. It is also
5 known that organic phosphorus flame retardants, which
are fluid at room temperature, have an adverse effect
on the polymer composition's stiffness.

The invention's object is hence a halogen-
free flame-retardant thermoplastic polyester or
10 polyamide composition that does not present the
aforementioned drawbacks, or possesses them to a
substantially lesser extent.

The invention's object is achieved with a
flame retardant combination that is characterised in
15 that the compound derived from triazine is a melamine
condensation product, preferably melam or melem. The
invention also covers a halogen-free glassfibre
reinforced thermoplastic polyamide composition in which
the flame retardant combination is characterised in
20 that the organic phosphorus compound contains at least
14 wt.% phosphorus and the compound derived from
triazine is melamine cyanurate.

In principle, all the current thermoplastic
polyesters and copolyesters and polyamides can be used
25 as the thermoplastic polyester or polyamide for the
composition. Examples of this are polyalkylene
terephthalates or copolyesters thereof with isophthalic
acid, for example polyethylene terephthalate, PET,
polybutylene terephthalate, PBT, polyalkylene
30 naphthalates, for example polyethylene naphthalate,
PEN, polypropylene naphthalate, polybutylene
naphthalate, PBN, polyalkylene dibenzoates, for example
polyethylene bibenzoate and copolyesters hereof.

Preferable are PET, PBT, PEN and PBN. Also suitable are block copolyesters which, in addition to hard polyester segments from the above group of thermoplastic polyesters, also contain soft polyester segments
5 derived from at least one polyether or aliphatic polyester. Examples of such block copolyesters with elastomeric properties are for example described in "Encyclopedia of Polymer Science and Engineering", Vol. 12, p.75 ff. (1988), John Wiley & Sons and
10 "Thermoplastic Elastomers", 2nd Ed., chapter 8 (1996) Hauser Verlag and the references mentioned therein.

Polyamides usefull in the practice of this invention include those which are well-known in the art, and for instance described in Encyclopedia op
15 Polymer Science and Technology, Vol. 11, p.315, (1988) ISBN 0-471-80943-8 (V.11). The invention is especially very effective in polyamides having a melting point of higher than 265°C. For instance polyamide 4.6 and the copolyamides based on aliphatic and aromatic
20 dicarboxylic acids. Examples thereof are polyamide 6/6.T, 6.6/6.T, 6.6/6/6.T, 6.6/6.I/6.T etc.

Melamine condensation products are for example melam, melem, melon and menthone and can for example be obtained with the process described in
25 WO-A-96/16948. Preferably the dimer, melam, or the trimer, melem, is used.

In the combination with a melamine condensation product the phosphorus compound can be chosen from the wide group of organic phosphates,
30 phosphites, phosphonates and phosphinates. Preferably use is made of phosphates and phosphonates. Examples of such compounds are described in for example Kirk Othmer, Encyclopedia of chemical technology, Vol. 10, p.396 ff. (1980).

- 4 -

A large number is commercially available, for example resorcinolbis(diphenylphosphate) oligomer, under the trade name Fyrolflex RDP from AKZO-Nobel, NL; cresyldiphenylphosphate, CDP, under the trade name
5 Kronitex CDP from FMC, UK; trimethylolpropanol ester of methyl phosphoric acid, under the trade name Amgard P45 from Albright and Wilson, USA; polypentaerythritol phosphonate under the trade name Cyagard RF 1041 from American Cyanamid, USA. Hostaflam OP 910; a mixture of
10 cyclic di- and triphosphonates containing 21 wt.% P, from Hoechst, Germany.

It is particularly advantageous to use an organic phosphorus compound with a phosphorus content of at least 14 wt.%; preferably 18 wt.%. An example of
15 this are Amgard P45, and the metal phosphinates as for instance in US-A-4,208,321 and US-A-3,594,347.

A practical requirement for the organic phosphorus compound is a low volatility at the processing temperatures of the polyester or polyamide
20 composition and the service temperature of objects obtained from the composition. For this reason cresyldiphenylphosphate, for example, is less suitable for guaranteeing flame-retardant behaviour in the longer term.

25 The compositions of the invention can be obtained in a simple way by means of mixing in the melt. Use is then preferably made of an extruder fitted with means that make it possible to dose the phosphorus compound, which is usually fluid at room temperature
30 already. It is also advantageous if fibrous reinforcing materials can be dosed to the melt separately. It is also possible that the flame retardant components are already present in the polymerisation process for the production of the polyamide or polyester.

The concentration of organic phosphorus compound may vary within a wide range, for example between 0.5 and 20 wt.%, preferably between 1 and 12 wt.%, even more preferably between 2 and 10 wt.%. The concentration of the compound derived from triazine may vary within a wide range, for example between 2 and 25 wt.%, preferably between 3 and 20 wt.%, most preferably between 4 and 16 wt.%. Weight percentages are relative to the composition's total weight. A person skilled in the art will be able to determine the optimum composition in his case through systematic research.

The compositions according to the invention may furthermore contain the usual additives, for example heat stabiliser, UV stabilisers, pigments, processing agents, for example mould release agents, and fillers, for example clay and reinforcing fibres, for example glass fibres. More substances that improve the flame-retardant behaviour may optionally be added, for example char-forming substances such as polyphenylene ether and polycarbonate and substances that have an effect on the dripping behaviour, for example fluoropolymers such as polytetrafluoroethylene. Well-known stabilisers are for example hindered phenols.

In the presence of glass fibre reinforcement in particular the compositions according to the invention show surprising advantages. For example, the CTI, comparative tracking index, increases from approx. 350 Volt to 600 Volt, which presents particular advantages in electrical applications. In addition, moduli of elasticity are realized that have never before been published for polyester and polyamide compositions based on organic phosphorus-containing

flame retardants with comparable flame-retardant behaviour.

The invention will now be further elucidated with reference to the following examples and 5 comparative examples.

Materials

- PBT, $\eta_{rel} = 2.0$, measured in m-cresol, from DSM, NL
- 10 PA-6 nylon-6, having a relative viscosity, $\eta_0 = 2.3$ (in formic acid)
- PA-6.6 nylon-6.6, having a relative viscosity, $\eta_0 = 2.4$ (in formic acid)
- 15 PA-4.6 Stanyl® KS 200, $\eta_0 = 2.3$ (in formic) of DSM
- PA-6.6/6.T/6.I Amodel® A 1133 HS, containing 33 wt% glassfibre, of AMOCO
- resorcinol(bis-biphenylphosphate), Fyroflex RDP®
- 20 from AKZO-Nobel. P content = 10.5 wt.%
- cresyldiphenylphosphate, Kronitex CDP, from FMC, USA. P content = 8.9 wt.%
- Zn-salt of dimethyl phosphonic acid, (DMPA) was prepared from DMPA from Aldrich and Zn-acetate. P
- 25 content = 22 wt.%.
- trimethylolpropanol ester of methylphosphoric acid, Amgard® P45, from Albright and Wilson, USA. P content = 20.8 wt.%
- melam from DSM, the Netherlands. Particle size d_{50}
- 30 = 4 μm
- melamine cyanurate from DSM, $d_{50} = 8 \mu m$
- glass fibre, length 4.5 cm, diameter 11 μm , PPG 3786 from PPG, France

Compounding

The compositions were mixed using a ZSK 30/39 D corotating twin-screw extruder with degassing at a set temperature of 250°C voor PBT and PA-6, 280°C for PA-6.6 and 300°C for PA 4.6 en PA 6.6/6.T/6.I. 10 kg/hour throughput at a speed of 200 rpm. Ground PBT or polyamide and solid components were premixed in dry condition and dried for 24 hours at 90°C. Glass fibre was dosed separately via a side feed. The fluid phosphorus compounds were injected with the aid of a dosing pump. Amgard P45 was to that end diluted with acetone.

15 Injection-moulding

Prior to the injection-moulding the granules obtained by compounding in the extruder were dried for 24 hours at 90°C.

An injection-moulding machine of type Engel 80 A was used for the injection-moulding at set temperatures of 235-245°C for PBT and PA-6, 280-300°C for PA 6.6 and 280-330°C for PA 4.6 and PA 6.6/6.T/6.I. The mould temperature was 90°C. Dimensions:

- UL-94 specimens: thickness 1.6 and 0.8 mm, resp.
- 25 - tensile test specimens: thickness 4 mm
- glow wire test plates: 1 mm thickness

Tests

The following properties of the injection-moulded specimens were determined:

30 **Flammability:** UL-94, GWFI (glow wire flammability test) according to ISO-IEC 695-2-1.

Mechanical properties: tensile test according to ISO 527/1 using dry-as-moulded samples.

Differential scanning calorimetry, DSC, was carried out at a scanning speed of 20°C/minute from -110°C to 250°C, after 10 minutes at 250°C, cooled at the same speed of 20°C/minute. The crystallisation temperature, T_c , was determined in the cooling curve, the melting point, T_m , was determined in the 2nd heating curve.

CTI, the comparative tracking index, was measured according to ISO IEC 112.

Compositions and results
They are given in Table 1 for PBT, as far as flame-retardant behaviour, mechanical properties, CTI and T_m - T_c are concerned.

TABLE 1

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
PBT 5007 [wt. %]	100	80	82.5	80	90	81	85	45	45	49	45	45	50	54
Mecy [wt. %]			10	12.5		15	7.5	15	15	15				
Melam [wt. %]											15	15	8	8
Fyroflex RDP [wt. %]				7.5				10			10			
CDP [wt. %]			7.5											
Angard P45 [wt. %]					10	4	7.5		10	6		10	12	
$[\text{Zn}(\text{CH}_2)_2\text{PO}_2]_x$														8
PPG 3786 [wt. %]		20						30	30	30	30	30	30	30

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
UL-94														
(1.6 mm 48 h. 23°C/50% RH)	N.C.	N.C.	V-0	V-0	V-2	V-0	V-0	N.C.	V-2	N.C.	N.C.	V-0	V-0	V-0
(1.6 mm 168 h. 70°C/50% RH)	.	.	V-0	V-0	V-2	V-0	V-0	-	V-2	N.C.	N.C.	V-0	V-0	V-0
(0.8 mm 48 h. 23°C/50% RH)			V-0	V-2	V-0	V-0	V-0	-	-	-	-	-	-	-
(0.8 mm 168 h. 70°C/50% RH)	N.C.	N.C.	-	-	V-2	V-0	V-0	-	-	-	-	-	-	-
GWFI (1 mm)	-	-	960	960	960	960	960	750	960	960	960	960	960	960
elongation at break [%]	100	3.5	23	17	9.4	3.2	5.4	3.1	2.0	2.2	2.8	2.5	2.5	2.8
E-modulus [N/mm ²]	2700	7000	1705	2036	2100	3100	2600	8200	8600	10300	8100	9600	10100	11000
tensile strength [N/mm ²]	55	120	37	40	53	53	51	85	92	105	80	105	110	118
CTI [Volt]	600	375	-	600	-	-	-	-	-	600	-	600	-	600
T _m -T _c	35- 40	-	-	36	-	-	-	-	15	17	-	30	-	-

SUBSTITUTE SHEET (RULE 26)

- 11 -

In Table 1 N.C. stands for 'no classification according to UL-94' (glow wire flammability test). If a measurement was not conducted, this is indicated by a dash: -.

- 5 The results obtained for the non-reinforced compositions reflect the superior effect of Amgard P45 relative to the RDP, in terms of the flame-retardant properties, tensile strength and stiffness.

- Composition 3 containing
10 cresyldiphenylphosphate, P content 8.9%, also showed good flame-retardant behaviour relative to composition 4, but coupled to a very low stiffness. These flame-retardant properties could however not be retained in time because the cresyldiphenylphosphate is too
15 volatile and gradually disappears with the composition. The advantages of Amgard P45 combined with melamine cyanurate are also clearly observable in glass-fibre reinforced compositions.

- In the glow wire flammability test (GWFI)
20 composition 8 was ignited at 750°C already; in the case of composition 10 with a substantially lower concentration of phosphorus-containing flame retardant this temperature is 960°C. A UL-94 classification V-2 can be obtained with composition 9 already.

- 25 When melam was used in composition 8 instead of melamine cyanurate (see composition 11), a GWFI of 960°C was measured. A UL classification of V-0 was realised for compositions 12 and 13. The great advantage in mechanical properties of the compositions
30 based on Amgard P45 is clearly observable here too (compositions 12 and 13).

 Also surprising is that the glass fibre reinforcement's adverse effect on the CTI (see

composition 2) was entirely counteracted in the composition according to the invention (10 and 12).

The compositions according to the invention also showed substantially better crystallisation
5 behaviour than the compositions according to the state of the art (EP-A-672717). The composition based on melamine cyanurate in particular offers particular advantages in that respect.

When instead of the Amgard P45 the Zn-salt of
10 dimethylphosphonic acid is used in the composition 13 the same flame retardant properties are measured. The mechanical properties are improved significantly.
(composition 14)

In Table 2 similar results are shown for
15 polyamides. Especially for the high melting polyamides the advantages of the combination of melamine condensation products and the phosphorus compound with a high phosphorous content are manifest. Actually it is, as far as is known by the inventors, the first time
20 that for the high melting glass fibre reinforced polyamides a non-halogen containing flame retardant composition is obtained fulfilling UL-94, V-O, that also possesses good mechanical and electrical properties.

25 In the highmelting polyamide the combination of a condensation product of melamine and a metal salt of a phosphinic acid is preferred. If the metal salt alone is been used in the polyamide only for a few metal salts and only in concentrations of at least
30 about 30 wt.% a V-O classification can be obtained for glass fibre reinforced compositions. In the combination with melam etc. with appreciably lower concentrations and for a great number of metals salts a high

classification can be realised, thereby giving better mechanical properties.

The compositions of the invention can be moulded into objects that can find wide application.

- 5 Very advantageous the compositions of the invention are used in the manufacture of electric and electronic parts.

Table 2

	15	16	17	18	19	20	21	22	23	24	25	26	27	28
PA-6	95	45	45											
PA-6.6				96	96	60	60	60	45					
PA-4.6										90	50	50	45	
PA 6.6/6.6.T/6.1														53
Mecy		15		4		20				*)				
Melam	5		15		4		20		15	10	20	12	15	12
Amgard P45		10	10					20	10				10	
$[\text{Zn}((\text{CH}_2)_2\text{PO}_2)_2]_x$												8		8
PPG 3786		30	30			20	20	20	30		30	30	30	27**)
UL-94 1,6 mm 48h 23°C/50% RH	V-O	NC	V-2	V-O	V-O	V-2	V-2	V-O	V-O	V-O	V-2	V-O	V-O	V-O
GWFI		960	850	960	960		960	960	960					
Elongation %		3.2	3.0						2,6					
E-modulus [N/mm ²] . 10 ³		10	10.8						11,3					

SUBSTITUTE SHEET (RULE 26)

	15	16	17	18	19	20	21	22	23	24	25	26	27	28
tensile strength [N/mm ²]		152	172			*)			176					
CTI [V]		-	-	-	-	-	500		600		450	550		550

*) not stable in compounding. T.S. inferior

**) origine glass fibre unknown.

SUBSTITUTE SHEET (RULE 26)

C L A I M S

1. Halogen-free flame-retardant glass fibre
reinforced thermoplastic polyamide composition
5 comprising a compound derived from triazine and an
organic phosphorus compound, characterised in that
the compound derived from triazine is melamine
cyanurate and the organic phosphorus compound
contains at least 14 wt.% phosphorus.
- 10 2. Flame-retardant polyamide composition according to
Claim 1, characterised in that the organic
phosphorus compound is a trimethylolpropanol ester
of methylphosphoric acid.
3. Flame-retardant polyamide composition according to
15 Claim 1 or Claim 2, characterised in that the
concentration of melamine cyanurate lies between 2
and 25 wt.% and the concentration of organic
phosphorus compound lies between 0.5 and 20 wt.%,
preferably between 3 and 20 wt.% and 1 and 12
20 wt.%, respectively.
4. Flame-retardant polyamide composition according to
Claim 3, characterised in that the concentration
of melamine cyanurate lies between 4 and 16 wt.%
and the concentration of organic phosphorus
25 compound lies between 2 and 10 wt.%.
5. Halogen-free flame-retardant thermoplastic
polyester or polyamide composition comprising a
compound derived from triazine and an organic
phosphorus compound, characterised in that the
30 compound derived from triazine is a melamine
condensation product.
6. Flame-retardant polyester or polyamide composition
according to Claim 5, characterised in that the
melamine condensation product is melam.

- 17 -

7. Flame-retardant polyester or polyamide composition according to Claim 5, characterised in that the organic phosphorus compound contains more than 14 wt.% phosphorus.
- 5 8. Flame-retardant polyester or polyamide composition according to any one of Claims 5-7, characterised in that the concentration of melamine condensate lies between 2 and 25 wt.% and the concentration of organic phosphorus compound lies between 0.5
10 and 20 wt.%, preferably between 3 and 20 wt.% and 1 and 12 wt.% of the composition, respectively.
9. Flame-retardant polyester or polyamide composition according to Claim 8, characterised in that the concentration of melamine condensate lies between
15 4 and 16 wt.% and the concentration of organic phosphorus compound lies between 2 and 10 wt.% of the composition.
10. Flame-retardant polyester or polyamide composition according to any one of the above claims,
20 characterised in that glass fibre reinforcement is also present.
11. Object moulded from a composition according to one of the claims 1-10.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 98/00226

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L67/00 C08L77/00 C08K5/00 //(C08K5/00,5:3492,5:54)

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 016, no. 106 (C-0919), 16 March 1992 & JP 03 281652 A (MITSUBISHI PETROCHEM CO LTD), 12 December 1991 see abstract ---	1-4,10
X	PATENT ABSTRACTS OF JAPAN vol. 017, no. 391 (C-1087), 22 July 1993 & JP 05 070671 A (MITSUBISHI PETROCHEM CO LTD), 23 March 1993 see abstract ---	1-4,10
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 485 (C-1248), 9 September 1994 & JP 06 157880 A (MITSUBISHI PETROCHEM CO LTD;OTHERS: 01), 7 June 1994 see abstract ---	1-4,10
-/--		

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"A" document member of the same patent family

Date of the actual completion of the international search

9 November 1998

Date of mailing of the international search report

19. 11. 1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Schueler, D

INTERNATIONAL SEARCH REPORT

Inter- nal Application No
PCT/NL 98/00226

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 096, no. 001, 31 January 1996 & JP 07 247410 A (TORAY IND INC), 26 September 1995 see abstract ---	1-4,10
X	PATENT ABSTRACTS OF JAPAN vol. 096, no. 007, 31 July 1996 & JP 08 073713 A (MITSUBISHI CHEM CORP), 19 March 1996 see abstract ---	1-4,10
X	PATENT ABSTRACTS OF JAPAN vol. 096, no. 007, 31 July 1996 & JP 08 081619 A (TORAY IND INC), 26 March 1996 see abstract ---	1-4,10
X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 002, 28 February 1997 & JP 08 269306 A (MITSUBISHI CHEM CORP), 15 October 1996 see abstract ---	1-4,10
X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 010, 31 October 1997 & JP 09 143350 A (KANEFUCHI CHEM IND CO LTD), 3 June 1997 see abstract ---	1-4,10
X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 010, 31 October 1997 & JP 09 143351 A (MITSUBISHI CHEM CORP;MITSUBISHI ENG PLAST KK), 3 June 1997 see abstract ---	1-4,10
X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 010, 31 October 1997 & JP 09 151305 A (MITSUBISHI CHEM CORP;MITSUBISHI ENG PLAST KK), 10 June 1997 see abstract ---	1-4,10
X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 010, 31 October 1997 & JP 09 157503 A (MITSUBISHI CHEM CORP;MITSUBISHI ENG PLAST KK), 17 June 1997 see abstract ---	1-4,10
P,X	DE 196 14 424 A (HOECHST AG) 16 October 1997 see claims 1-3,5,6 ---	1-4,10
-/--		

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 98/00226

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 97 42264 A (T & N TECHNOLOGY LTD ; MARTIN LEE HAMILTON (US)) 13 November 1997 see claims 1-4	1-4, 10
A	DD 135 207 A (KEIL MARTIN; PAPE DIETER; VOGT HANS; JECHT WERNER; HELD ROLF WYLAND; MA) 18 April 1979 see claim 2; example 5	5

INTERNATIONAL SEARCH REPORT

In. .ational application No.
PCT/NL 98/00226

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such
an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all
searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment
of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report
covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is
restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/NL 98/00226

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-4 10 11

polyester composition characterised by
a) melamincyanurate with a number of N-atoms of 9;
number of O-atoms 3;
b) phosphoric compound with a P-content > 14 wt%

2. Claims: 5-9

polyester or polyamide composition characterised by
a) melamine-condensate with a number of N-atoms 10,
number of O-atoms 0;
b) phosphoric compound of undefined P-content;
compound a) showing therefore totally different chemical
behaviour, characteristics and properties than the compound
a) disclosed in invention part 1

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/NL 98/00226

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 19614424 A	16-10-1997	AU 2293997 A WO 9739053 A	07-11-1997 23-10-1997
WO 9742264 A	13-11-1997	GB 2312900 A	12-11-1997
DD 135207 A	18-04-1979	NONE	